

# इंटरनेट

# मानक

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IS 6212 (1992): Determination of thiosulphate and other residual chemicals in processed photographic films, plates and papers [CHD 5: Electroplating Chemicals and Photographic Materials]



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भारतीय मानक

संसाधित फोटोग्राफिक फिल्मों, प्लेट तथा  
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ज्ञात करने की परीक्षण पद्धति  
( पहला पुनरीक्षण )

*Indian Standard*

DETERMINATION OF THIOSULPHATE AND  
OTHER RESIDUAL CHEMICALS IN  
PROCESSED PHOTOGRAPHIC FILMS,  
PLATES AND PAPERS — METHOD OF TEST  
( *First Revision* )

UDC 771.531/3 : 543 : 546.233.2

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NEW DELHI 110002

## FOREWORD

This Indian Standard ( First Revision ) was adopted by the Bureau of Indian Standards, after the draft finalized by the Photographic Materials Sectional Committee had been approved by the Chemical Division Council.

This standard is one of a series of specifications on photographic processing. Determination of the amount of residual thiosulphate ( and its decomposition products that can form silver sulphide ) in processed photographic films, plates and papers is of use in appraisal of the adequacy of washing, which is an important factor affecting image stability on storage.

This standard was first published in 1971. In this standard the mercury ( II ) bromide method was stipulated and only black and white photographic plates were covered. It was found that this method is not sufficiently reproducible. An additional disadvantage being that the analysis has to be carried out within 24 h of processing.

In this revision the methylene blue method which does not suffer from these disadvantages has been prescribed. An additional method, namely silver sulphide method has also been specified. Both these methods are applicable to both colour as well as black-and-white products.

This standard has been based on ISO 417 : 1977 Photography—Determination of thiosulphate and other residual chemicals in processed photographic films, plates and papers—Methylene blue photometric method and silver sulphide densitometric method, published by the International Organization for Standardization.

If more than two weeks have elapsed between processing and analysis, some degradation of residue thiosulphate into polythionates or sulphide may have occurred. Valid analysis may be obtained on such samples with either of two test methods, but it must be recognized that the result might have been higher if the analysis had been carried out within two weeks of processing.

The silver sulphide method is not affected as much by the time-lapse before analysis because it measures polythionate decomposition products in addition to the thiosulphate.

The methylene blue method, on the other hand, measures only the thiosulphate, and should be carried out within two weeks of processing.

Residual thiosulphate is particularly objectionable in the minimum density areas because of its likelihood of producing yellow stain on ageing. Either of these methods will determine residual thiosulphate down to  $0.7 \mu\text{g}/\text{cm}^2$ , and results from either method may be correlated with ageing test results. However, the conversion of density values from the silver sulphide method into the equivalent amount of thiosulphate involves risk, this being least with results from freshly processed samples. If, in spite of this risk, one wishes to use the silver sulphide method and convert the results to thiosulphate content, freshly processed samples covering a range of thiosulphate contents should be analysed by both methods. A calibration graph can then be drawn, but this should be used only for materials similar to that used in its construction.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values ( revised )'.

## Indian Standard

# DETERMINATION OF THIOSULPHATE AND OTHER RESIDUAL CHEMICALS IN PROCESSED PHOTOGRAPHIC FILMS, PLATES AND PAPERS — METHOD OF TEST ( *First Revision* )

## 1 SCOPE

1.1 This standard specifies two methods for determination of residual thiosulphate in processed films, plates and papers, namely a methylene blue photometric method and a silver sulphide densitometric method. The methods are not applicable to stabilized black-and-white products.

1.2 The methylene blue method measures only thiosulphate. Procedures are specified to cover the range 0.1 to 45  $\mu\text{g}$  of thiosulphate ion per square centimetre. The sample must be tested within two weeks of processing.

1.3 The silver sulphide method measures thiosulphate, polythionates and all other residual chemicals that react with the silver ion to give silver sulphide under the conditions of the test. The results are reported as optical densities, and the density increase due to the residual chemicals should be at least 0.03, this value corresponding approximately to 0.7  $\mu\text{g}/\text{cm}^2$ . Test results from this method may be converted to thiosulphate concentration if a correlation graph is

first established for the particular type of material being tested.

## 2 METHYLENE BLUE METHOD

### 2.1 Outline of the Method

Residual thiosulphate eluted from the sample is reduced by potassium borohydride to sulphide. The sulphide then reacts with *N,N*-dimethyl-*p*-phenylenediamine to form methylene blue. The absorbance of the blue colour is measured with a photometer or spectrophotometer, and the thiosulphate concentration is read from a calibration graph. This calibration graph should be prepared in each laboratory to eliminate errors due to variations in reagents, equipment or technique, and should be similar to that shown in Fig. 1.

### 2.2 Coating on Each Side of the Base

Films or plates with a gelatin layer on each side after processing shall contain approximately twice as much residual thiosulphate as materials with such layer on one side only.

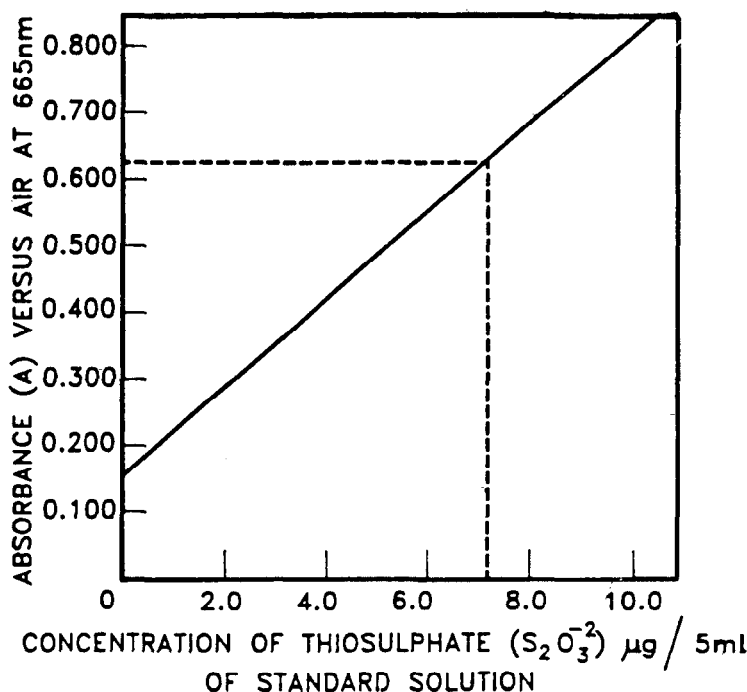


FIG. 1 TYPICAL CALIBRATION GRAPH FOR THE METHYLENE BLUE TEST METHOD

NOTE — See example 3 under 2.8.4 for the method of reporting the results for such materials.

## 2.3 Selection of Procedure to Cover Correct Ranges

Two procedures are specified which permit a wide range of concentrations to be covered. The range of procedure I is 0.1 to 0.9 µg of thiosulphate per square centimetre and that of procedure II is 0.9 to 45 µg of thiosulphate per square centimetre. In both procedures, the sample sizes and volumes of test solution are such that not more than 10 µg of thiosulphate are present, thus ensuring a straight-line calibration graph. The use of the large volume of eluent for procedure II is preferable to the use of a smaller sample size, which could reduce the precision of the test.

## 2.4 Reagents

Reagents used in the test procedure shall meet the specifications for reagent grade chemicals where possible. If no such specification exists, the purity shall be that generally used for careful analytical work. The establishment of a calibration graph similar to that given in Fig.1 will generally indicate that reagent purity is satisfactory.

Whenever water is specified, it shall be distilled or deionized water. Care shall be taken in using water that has passed through copper pipes, as copper contamination will reduce sensitivity.

### 2.4.1 Eluent

Dissolve 1.0 g of potassium iodide, 20.0 g of potassium bromide and 1.0 g of potassium dihydrogen phosphate in 1 000 ml of water.

This reagent is stable for at least 8 months.

### 2.4.2 Borohydride Reagent

**CAUTION** — Hazardous to personnel and to sensitized materials.

(See NOTE)

Dissolve 3.0 g of fresh potassium borohydride ( $\text{KBH}_4$ ) in 100 ml of approximately 0.2 M sodium hydroxide solution.

This reagent is stable for 1 week in a cool place. (Sodium borohydride should not be used because it is hygroscopic and unstable in the solid state.)

NOTE — Potassium borohydride is inflammable; it liberates hydrogen in contact with water or dilute acid. It liberates poisonous gases in the presence of acid and causes severe skin burns in concentrated forms. It should be handled with extreme care. Potassium borohydride is a powerful fogging agent. Avoid contamination of unprocessed film and developers. Thoroughly wash hands and equipment after use of borohydride.

### 2.4.3 Acetone

### 2.4.4 Iron (III) Sulphate Reagent

To 89 ml of water in a beaker, carefully add, with stirring, 15 ml of concentrated sulphuric acid. Dis-

solve 3.00 g of hydrated iron (III) sulphate in the diluted acid.

This reagent is stable for at least 8 months.

### 2.4.5 *N, N*-Dimethyl-*p*-Phenylenediamine Sulphate Reagent (NND)

**CAUTION** — Acid — Avoid contact with skin and eyes. In case of contact flush copiously with water.

To 89 ml of water in a beaker, carefully add, with stirring, 15 ml of concentrated sulphuric acid. Dissolve 1.00 g of NND in the dilute acid, add 5 g of powdered silica gel and stir the mixture until all coloured material is adsorbed. Allow the adsorbent to settle and decant the supernatant solution for use.

This reagent is stable for at least 8 months.

### 2.4.6 Sodium Thiosulphate — approximately 0.1 M solution.

Dissolve 24.8 g of sodium thiosulphate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in about 500 ml of water and make up to 1 000 ml. No standardization is necessary.

## 2.5 Apparatus

### 2.5.1 Tubes

10-ml tubes with polyethylene caps for films and papers.

### 2.5.2 Glass or Plastic Trays for Plates

The trays shall be slightly larger than the plates to be eluted.

### 2.5.3 Visible Range Spectrophotometer or Filter Photometer

## 2.6 Methylene Blue Procedure I

### 2.6.0 General

This is for the low range (0.1 to 0.9 µg of  $\text{S}_2\text{O}_3^{2-}$  per square centimetre) which is attained with well-washed, fine-grain, black and white films and plates. For higher amounts, use procedure II or the silver sulphide method. If the sample has a gelatin backing, the backing may contain as much thiosulphate as the emulsion. The test method measures the total thiosulphate.

### 2.6.1 Films and Non-absorbent Papers

Take a 10 cm<sup>2</sup> sample from a minimum density area, fold into a W-shape and place in a 10-ml tube (see 2.5.1). Add 5.0 ml of the eluent (see 2.4.1) and allow to stand for 20 minutes at room temperature with occasional swirling. Remove the sample with tweezers and drain carefully. (Prints on the usual paperbase generally contain too much thiosulphate for procedure I.)

### 2.6.2 Plates

Take a 10 cm<sup>2</sup> sample from a minimum density area and place, emulsion layer up, in a glass or plastic tray (see 2.5.2) slightly larger than the sample. Add 5.0 ml

of eluent and allow to stand for 20 min at room temperature with occasional rocking. Then pour off the eluent into a 10- ml tube.

**2.6.3** Fill four medicine droppers with the reagent in readiness for the additions to the solutions obtained in 2.6.1 or 2.6.2.

**2.6.4** Add 5 drops of the borohydride reagent (see 2.4.2). Swirl to mix, wait for 5 seconds and proceed immediately to the next step.

**2.6.5** Add 10 drops of acetone (see 2.4.3). Swirl to mix. Wait for 5 seconds and proceed to the next step without delay.

**2.6.6** Add 5 drops of the iron (III) sulphate reagent (see 2.4.4) and 5 drops of the NND reagent (see 2.4.5). Cap immediately.

**2.6.7** Hold the cap on firmly and shake the tube vigorously for 30 seconds. Vent the pressure formed by any evolved hydrogen. Re-cap the tube, shake it vigorously again for 30 seconds and vent. Allow the test solution to stand until the red colour (Wurster's salt has disappeared (3 to 5 minutes). If no red colour has formed, the thiosulphate content is too high, in which case repeat by procedure II.

**2.6.8** Read the absorbance of the test solution in the spectrophotometer or filter photometer (see 2.5.3) at a wave-length of 665 nm against an air blank. If the absorbance is greater than 0.800, discard the test and retest by procedure II.

**2.6.9** From the calibration graph, read the amount of thiosulphate ion per 5 ml of test solution from its absorbance. To obtain the number of micrograms of  $S_2O_3^{2-}$  per square centimetre, divide the value by 10 as the sample area was 10  $cm^2$ . If the thiosulphate is required as sodium thiosulphate, anhydrous, multiply by 1.4 (see example 1 under 2.8.4). For double-sided materials, the result should be divided by 2 to obtain the amount per side (see example 3 under 2.8.4).

## 2.7 Methylene Blue Procedure II

### 2.7.0 General

This procedure is applicable for the high range (up to 45  $\mu g$  of  $S_2O_3^{2-}$  per square centimetre).

**2.7.1** Extract a new 10  $cm^2$  sample of film, plate or paper in 25 ml of eluent (see 2.4.1) and allow to stand for 20 min at room temperature with occasional swirling. Remove the sample.

**2.7.2** Pipette out 5 ml of the test solution into a 10-ml tube (see 2.5.1) and continue as under Procedure I, 2.6.3 to 2.6.7.

**2.7.3** Read the absorbance of the test solution in the spectrophotometer or filter photometer (see 2.5.3) at a wave-length of 665 nm. This should be below 0.8. Read the thiosulphate content from the calibration graph.

**2.7.4** To obtain the number of micrograms of  $S_2O_3^{2-}$  per square centimetre of sample, multiply by 0.5 (see example 2 under 2.8.4).

**2.7.5** If the absorbance is above 0.8, the thiosulphate content is above 4.5  $\mu g/cm^2$ . In this case, use a more dilute test solution by following 2.7.6.

**2.7.6** Pipette out 10 ml of the solution prepared in 2.7.1 into a 100-ml volumetric flask and dilute to the mark with fresh eluent.

**2.7.7** Pipette out 5 ml of this diluted solution into a 10-ml tube and continue from 2.6.3 to 2.6.7.

**2.7.8** Read the absorbance at 665 nm. This should be below 0.8.

**2.7.9** Read the amount of thiosulphate from the calibration graph.

**2.7.10** To obtain the number of micrograms of  $S_2O_3^{2-}$  per square centimetre of sample, multiply by 5.

**2.7.11** If the absorbance is above 0.8, the thiosulphate content exceeds 45  $\mu g/cm^2$ .

**2.7.12** If the sample has a coating on each side, report the results as in example 3 of Fig. 1.

## 2.8 Methylene Blue Method Calibration Graph

### 2.8.1 Preparation of Standard Thiosulphate Solution

This must be prepared on the day of use. Pipette out 25.0 ml of sodium thiosulphate solution (see 2.4.6) into a 500-ml volumetric flask and dilute to the mark with water. Stopper and mix. Pipette out 5.0 ml of this solution into a 250-ml volumetric flask and dilute to the mark with water. Stopper and mix. The resulting solution contains 11.2  $\mu g$  of  $S_2O_3^{2-}$  per millilitre.

**2.8.2** Fill a 10-ml burette with the 11.2  $\mu g/ml$  standard thiosulphate solution.

Fill a 25-ml burette with fresh eluent. Make four standard mixtures in 10-ml tubes according to the volumes given in Table 1.

**Table 1 Preparation of Standard Solutions for Calibration**

Tube No.	Volumes of Reagents, ml		Content of Standard solution  $\mu g S_2O_3^{2-}/5 ml$
	Standard Thiosulphate Solution 11.2 $\mu g S_2O_3^{2-}/ml$	Eluent	
1	0.20	4.8	2.2
2	0.40	4.6	4.5
3	0.60	4.4	6.7
4	0.80	4.2	9.0



**2.8.3** Treat each standard solution as in steps 2.6.3 to 2.6.8.

**2.8.4** Plot the absorbance obtained against thio-sulphate concentration. The graph should be similar to that shown in Fig. 1 but may curve above a density of 0.4.

*Example 1 :* Using procedure 1: If a 10 cm<sup>2</sup> film sample has an absorbance of 0.632, it corresponds to 7.2 µg of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> per 5 ml of test solution. The film then contains 0.7 µg S<sub>2</sub>O<sub>3</sub><sup>2-</sup>/cm<sup>2</sup>.

*Example 2 :* Using procedure II: If a 10 cm<sup>2</sup> sample has an absorbance of 0.400, it corresponds to 4.1 µg of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> per 5 ml of test solution. The sample then contains 2.0 µg S<sub>2</sub>O<sub>3</sub><sup>2-</sup>/cm<sup>2</sup>.

*Example 3 :* Using either procedure: If the sample has gelatin on each side, it is assumed that the residual S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is equally divided between the two sides. Therefore, the number of micrograms of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> per square centimetre on each side will be one-half the total. For example, if the sample in example 2 has a gelatin backing, the concentration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is 1.0 µg/cm<sup>2</sup> of emulsion.

### 3 SILVER SULPHIDE METHOD

#### 3.1 Outline of Test

A strip of film, plate or paper is immersed to half its length in an acidified silver nitrate reagent. Thiosulphate and certain other ions, if present, will produce a yellow-brown stain. The complete strip is then immersed in a sodium chloride solution followed by a thiosulphate/sulphite fix to remove the excess silver ions. After washing and drying, the densities of the stained and unstained areas of the sample are measured. On film and plate samples, two thicknesses are used. The difference in densities is a measure of the residual chemicals. The results are reported as density differences.

#### 3.2 Reagents

Reagents used in the test procedure shall meet the

specifications for reagent grade chemicals. If no specification exists, the purity shall be that generally used for careful analytical work.

Whenever water is specified, it shall be distilled or deionized water.

##### 3.2.1 Silver Nitrate — Acetic Acid Reagent.

Dissolve 10 g of silver nitrate in a solution containing 30 ml of glacial acetic acid in 750 ml of water. Dilute to 1 000 ml and store in a brown, glass-stoppered bottle away from strong light. Discard the reagent if it has darkened.

**CAUTION** — Silver nitrate is caustic and irritating to skin and mucous membranes. It is also poisonous and ingestion should be avoided. Also avoid contact of glacial acetic acid with skin and eyes. In case of contact, flush copiously with water.

##### 3.2.2 Sodium Chloride Reagent

Dissolve 50 g of sodium chloride in water and dilute to 1 000 ml.

##### 3.2.3 Sodium Thiosulphate — Sodium Sulphite Reagent.

Dissolve 19 g of sodium sulphite, anhydrous, and 50 g of sodium thiosulphate, pentahydrate in 750 ml of freshly boiled and cooled water. Dilute to 1 000 ml.

#### 3.3 Apparatus

Transmission densitometer for films and plates and a reflection densitometer for papers. All measurements shall be made through a blue-green filter having the transmission characteristics shown in Table 2.

#### 3.4 Procedure

##### 3.4.1 Sample Preparation

For films, cut a strip of about 1.5 cm × 6 cm from a minimum density area and fold at the mid-point with the emulsion side out.

**Table 2 Transmission Characteristics of Blue-Green Filter**

(Clause 3.3)

Wavelength (nm)	Transmittance (%)	Wavelength (nm)	Transmittance (%)
310	1	710	13
320	28	720	17
330	53	730	22
340	69	740	25
350	78	750	27
360	80	760	21
370	77	770	14
380	61	780	11
390	24	790	10
400 to 700	1	800	10

For plates, cut two pieces of about 1.5 cm × 3 cm from a minimum density area.

For papers, cut a piece of about 1.5 cm × 3 cm from a minimum density area.

### 3.4.2 Treatment

Immerse one-half of the sample (for film, folded end down) in 20 ml of the silver nitrate-acetic acid reagent (see 3.2.1) for 4 minutes with occasional agitation. Remove and immerse the whole sample in 20 ml of the sodium chloride reagent (see 3.2.2) for 4 minutes with occasional agitation. Remove and immerse the whole sample in 20 ml of the sodium thiosulphate-sodium reagent (see 3.2.3) for 4 minutes with occasional agitation.

Remove and wash the sample under running tap water for about 10 minutes and then dry.

### 3.4.3 Density Measurement

For film, refold the dry strip with the emulsion side out. Measure, to the second decimal place, the density of

the double thickness of film in both the stained and unstained areas, using the transmission densitometer (see 3.3) and the prescribed filter.

For plates, measure the densities of the two pieces, superimposed, in a similar manner.

For paper, measure the densities of a single thickness, using the reflection densitometer (see 3.3) and the prescribed filter.

Subtract the density of the unstained area from that of the stained area, and report the results as density differences, for example,  $\Delta D = 0.13$ . Density differences below 0.03 should be ignored.

### 3.4.4 Conversion to Thiosulphate Content

Although there may not be universal correlation between the density produced and the thiosulphate content (as measured by the methylene blue method), a correlation graph can be constructed and used for a specific product. For optimum correlation, the determinations should all be carried out on freshly processed samples. An example of such a correlation graph is shown in Fig. 2.

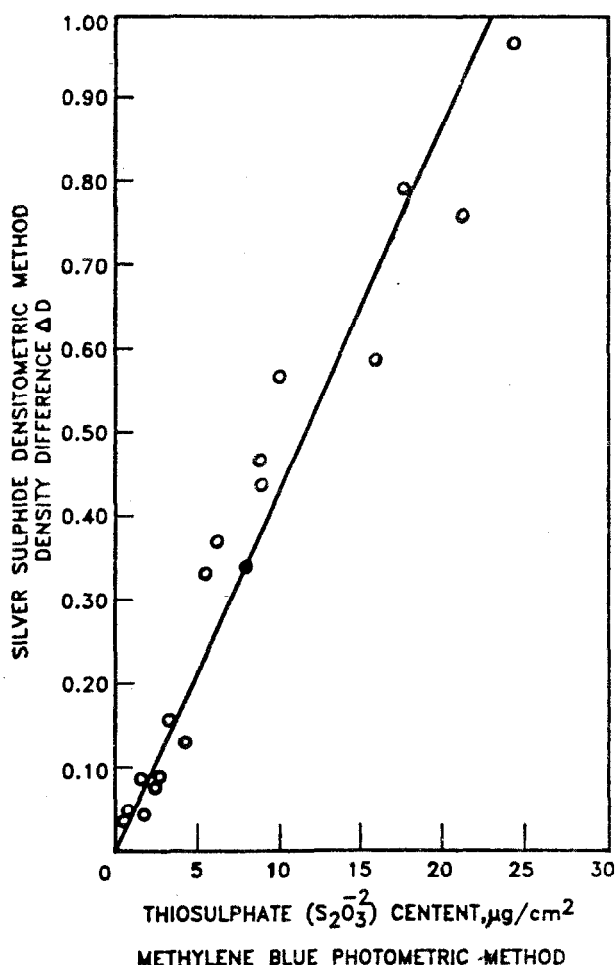


FIG. 2 ILLUSTRATIVE CORRELATION BETWEEN RESULTS OBTAINED BY SILVER SULPHIDE DENSITOMETRIC METHOD AND METHYLENE BLUE PHOTOMETRIC METHOD FOR DETERMINATION OF THIOSULPHATE

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#### Amendments Issued Since Publication

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